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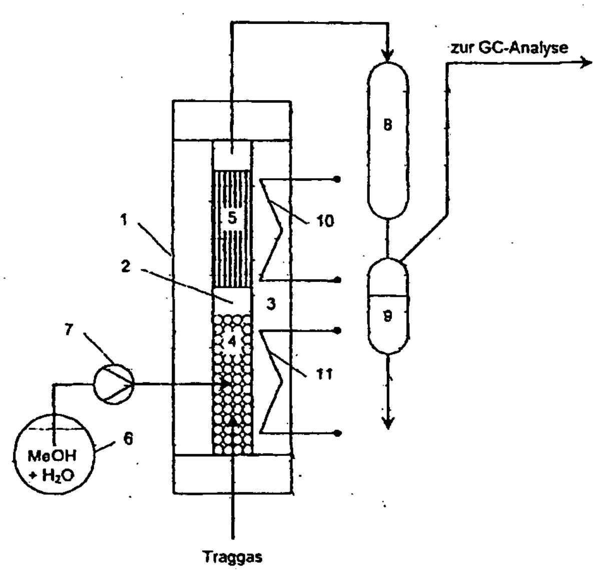
(54) **Catalyst for the Steam Re-forming of Alcohols**

(57) The invention concerns a catalyst for the steam re-forming of alcohols, which contains a palladium/zinc alloy and zinc oxide as catalytically active components. The catalyst alloy is characterized by the fact that the catalytically active components are precipitated on at least one carrier material of the group aluminum oxide, aluminum silicate, titanium oxide, zirconium oxide, zeolite, and mixtures or mixed oxides of the same.



Figur 1

Description

[0001] The invention concerns a catalyst for the steam re-forming of alcohols, which contains a palladium/zinc alloy and zinc oxide as catalytically active components. The catalyst is used in particular for the steam re-forming of methanol to produce a hydrogen-rich gas that can be used as a fuel for vehicles that are driven with fuel cells.

[0002] The steam re-forming of methanol in the presence of catalysts is a known method for production of hydrogen-rich gas mixtures, on which the following endothermic reaction is based:

Steam Re-forming of Methanol

[0003]

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \ \Delta H > 0 \qquad (1)$$

[0004] Here there may be the following secondary reactions.

Re-forming of Methanol by Methanol Splitting

[0005]

$$CH_3OH \rightarrow CO + 2H_2 \ \Delta H > 0 \qquad (2)$$

and

CO-Conversion

[0006]

$$CO + H_2O \leftrightarrow CO_2 + 3H_2 \ \Delta H < 0 \qquad (3)$$

[0007] In steam re-forming in accordance with the reaction equation (1), excess steam is used. To characterize the excess of water that is used, the so-called steam/carbon ration (S/C) is used. Usually a value for S/C between 1.2 and 2.0 is selected. In the case of re-forming of methanol, the S/C value is identical to the molar ratio of water to methanol.

[0008] For use in fuel cells, gas mixtures are needed that have a high hydrogen content and a low carbon monoxide content, since carbon monoxide deactivates the anode catalyst at which the oxidation of the fuel occurs. Usually the carbon monoxide content of the fuel is kept below 100 ppm, preferably less than 10 ppm.

[0009] If the fuel is obtained from re-forming methanol, then this requirement currently is met only by means of a post-processing cleaning of the re-format gas. The expense associated with this becomes lower as the carbon monoxide content of the re-format gas is decreased.

[0010] In the case of use in vehicles, it is necessary for space and weight reasons to have re-form catalysts that have a very high specific hydrogen productivity and a high selectivity, whereby for characterizing the selectivity of the steam re-forming, one draws upon the selectivity of the formation of carbon dioxide.

[0011] In the framework of this invention, specific hydrogen productivity P_{Kat} of the catalyst is understood to be the volume of hydrogen V_{H2} produced per mass M_{Kat} of the catalyst and reaction time t, whereby the catalyst mass is given in kilograms, the reaction time in hours, and the volume in standard cubic meters.

$$P_{Kat} = \frac{V_{H2}}{M_{Kat} \bullet t} \left[\frac{Nm^3}{kg_{Kat} \bullet h} \right] \quad (4)$$

[0012] The carbon dioxide selectivity S_{CO2} of steam re-forming is calculated with the help of the partial pressure of the carbon dioxide formed p_{CO2} and carbon monoxide p_{CO} as follows:

$$S_{CO2} = \frac{p_{CO2}}{p_{CO2} + p_{CO}} [\%] \quad (5)$$

[0013] A high specific activity is the precondition for obtaining a high space-time yield, which makes it possible to keep the reactor volume of the steam re-forming small. With high selectivity one can also decrease the space needed for gas purification.

[0014] The patent EP 0687648 A1 describes a two-stage method for conducting methanol re-forming, whereby in the first stage the methanol is reacted only incompletely in a heat transfer optimized process at a high specific load of the catalyst, and thereafter a reaction that completes the methane volume conversion in an optimized second stage with a lower specific load of the catalyst. In the first stage the catalyst is loaded as high as possible, preferably with more than 10 Nm^3/h H_2 per kilogram of catalyst. Catalysts that are recommended are pellet catalysts and also catalysts with layered metal sheets.

[0015] For methanol re-forming, the majority of the catalysts that are used have low-grade metals, such as copper, zinc, chromium, iron, cobalt, and nickel. Particularly beneficial are catalysts based on CuO/ZnO, with which selectivities of more than 95% can be achieved. There are catalysts known that consist entirely of CuO and ZnO and that can be obtained for example by co-precipitation from a solution of copper nitrate and zinc nitrate. After co-precipitation, the material that is obtained is usually calcined in air in order to decompose the compounds of metals that have precipitated out and to convert them into the corresponding oxides. Finally, the catalyst is reduced, for example, in the gas phase.

[0016] Alternatively, so-called carrier catalysts come into use, in which a porous carrier or a finely distributed, porous carrier material is impregnated with solutions of copper nitrate and zinc nitrate, calcined, and reduced. In these cases, the carrier or carrier material that is used is primarily aluminum oxide, but even zirconium oxide, titanium oxide, and zeolite is used.

[0017] The finely distributed particle catalyst materials obtained in this manner are machined as a rule to spherical bodies, so-called pellets, or deposited in the form of a layer on a carrier body. To differentiate them from pellet catalysts, the latter catalysts are designated in the following as coating catalysts. Methods that are known from the production of monolithic automotive exhaust catalysts are used, for example, for coating carrier bodies. To do this, the finely distributed particle catalyst material is dispersed for example in water, in some cases with the addition of suitable bonding agents. The carrier bodies are then coated by dipping into the coating dispersion with the catalyst material. To fix the coating on the carrier body, it is dried and then calcined.

[0018] The carrier body for the coating catalysts serves only as a substrate for the catalytically active coating. In this case it is a matter of macroscopic bodies that should not be mistaken for the carrier material for catalytically active compounds. Materials that are suitable for carrier bodies include heat exchanger sheets or honeycomb bodies of ceramic or metal foil. For

example, here one can also use the honeycomb material of cordierite used for exhaust treatment of combustion motors. They possess axis-parallel flow channels for reagents that are arranged in a narrow screen across the cross section. The number of flow channels per area of cross section is termed cell density. The wall surfaces of these flow channels bear the catalyst coating.

[0019] From DE 19721751 C1 and EP 0884273 A1 it is known that catalysts based on CuO/ZnO show a contraction of up to 40% in operation and a decrease in specific activity. DE 19721751 C1 solves this problem of contraction in the catalyst layers on a metal sheet by applying expansion joints in the layers. According to EP 0884273 A1 the yielding activity of a pellet fill of a Cu/ZnO catalyst on a carrier made of aluminum oxide can be reversed at least in part by periodic regeneration.

[0020] In JP 57007255 A2 (according to CA 96:145940), catalysts are described that are obtained by a two-stage impregnation of an aluminum oxide pellet coated with zirconium oxide using one or two metals or metal oxides of copper, zinc, chromium, iron, cobalt, nickel, and with platinum or palladium. A typical catalyst contains 10 weight percent palladium and 20 weight percent zirconium oxide on the pellet of aluminum oxide.

[0021] Besides catalysts based on metals that are not high grade, noble metals of the platinum group, in particular platinum, palladium, and rhodium on oxide carrier materials such as aluminum oxide, titanium oxide, and zirconium oxide are used for the re-formation of methanol. These catalysts lead to methanol splitting according to reaction equation (2) with a carbon monoxide content of product gas of up to 33 volume percent. Such catalysts are hardly suited for steam re-forming of methanol. As examples, one can note EP 0201070 A2, JP 60137434 A2 (according to CA 104: 185977), JP 04362001 A (according to WPI 93-033201) and JP 03196839 A (according to WPI 91-298480).

[0022] JP 60082137 describes a catalyst for methanol splitting that contains at least one of the noble metals platinum and palladium on a carrier of aluminum oxide, whereby the carrier is coated in a pretreatment phase with zinc oxide and / or chromium oxide. As a precoating the carrier is impregnated with an aqueous solution of zinc nitrate and / or chromium nitrate, and then calcined. Thereafter, the pretreated carrier is impregnated with an aqueous solution of a noble metal compound, dried, calcined, and reduced under hydrogen.

[0023] It is further known that catalysts that contain palladium on a carrier of zinc oxide can also be used for steam re-forming of methanol. In "Highly selected supported Pd catalysts for steam reforming of methanol," Catal. Lett. 19, (1993) pp. 211-216, N. Takezawa et al. examined the dependence of specific selectivity of different powder catalysts of palladium on zinc oxide. The catalysts are produced by impregnation by zinc oxide with palladium nitrate $Pd(NO_3)2$, drying, and calcination for 3 hours at 500 C in air. Powder catalysts with a palladium load of 1 weight percent show a high selectivity for carbon dioxide of 97%. The hydrogen productivity amounts at any rate to only 0.6 $Nm^3/(kg \cdot h)$.

[0024] In JP 05049930 A, powder catalysts of palladium and zinc oxide are described that are produced by co-precipitation of palladium nitrate and zinc nitrate and subsequent calcination at 500 C. The greatest hydrogen productivity of 2.7 $Nm^3/(kg \cdot h)$ at 220 C is obtained with a catalyst that has 15 weight percent palladium.

[0025] N. Takezawa et al. indicate in "*Steam reforming of methanol over Pd/ZnO: Effect of PdZn alloys upon reaction*," Appl. Catal. A 125, 1995, pp. 145-157, that the catalytic function of

palladium/zinc oxide catalysts can be clearly improved by the formation of a PdZn alloy. For the production of such a catalyst, first zinc oxide is impregnated with palladium nitrate, dried, and calcined at 500 C in air for a period of 3 hours. The PdZn alloy is formed by the reduction of the catalyst at increased temperatures. The studies of Takezawa show that the alloy formation is completed only at reduction temperatures of 500 C. Catalysts that are treated in this manner possess a very high selectivity, but a clearly lower activity than known copper/zinc oxide catalysts $Cu/ZnO/Cr_2O_3$ (30 weight percent Cu) and $Cu/ZnO/Al_2O_3$ (30 weight percent Cu). N. Takezawa describes a detailed examination of PdZn alloys in "*Selective PdZn alloy formation in the reduction of Pd/ZnO catalysts*," Bull. Chem. Soc. Jpn., 71, 1451-1455 (1998).

[0026] In "*Steam reforming of methanol over Ni, Co, Pd, and Pt supported on ZnO*," React. Kinet. Catal. Lett. Vol. 55, No. 2, pp. 349-353, it is shown that besides Pd/ZnO, also Pt/ZnO possesses a high selectivity for the steam re-forming of methanol.

[0027] In "*New catalytic functions of Pd-Zn, Pd-Ga, Pd-In, Pt-Zn, Pt-Ga, and Pt-In alloys in the conversions of methanol*," Catal. Lett. 54 (1998), pp. 119-123, N. Takezawa et al. describe catalysts for re-forming methanol based on alloys of the type Pd-Zn, Pd-Ga, Pd-In, Pt-Zn, Pt-Ga, and Pt-In. Of the catalysts tested, Pd/ZnO at 220 C shows the greatest selectivity and activity during the steam re-forming of methanol.

[0028] The known catalysts for steam re-forming of methanol on the basis of palladium on formation of a palladium-zinc alloy. The specific hydrogen productivities determined from the published data, namely a maximum of 2.7 $Nm^3/kg \cdot h$ require further improvement, however. Besides this, the types of catalysts that are described here are powder catalysts, which are poorly suited for application in methanol re-formers in vehicles.

[0029] Catalyst powders can in fact be worked chiefly to form bodies such as, for example, tablets or spheres, and then applied in the form of a catalyst fill; however, the more difficult accessibility of the reactants to the catalytically active centers inside the form bodies automatically diminishes the hydrogen production and consequently the achievable time – space yield. This has corresponding negative effects on the volume of the reactor that is needed. The binder that is in some cases necessary for shaping diminishes the hydrogen production even further. The vibrations produced by operating the vehicle lead furthermore to an undesired friction of the form bodies, which blocks the flow paths in the fill and thus increases the pressure drop in the reactor continuously.

[0030] A remedy might be offered by the coating catalysts mentioned here. However, coating tests conducted by the inventors have shown that Pd/ZnO catalyst powders lead to a thixotropic coating dispersion due to their basicity, which can be handled only with difficulty and which leads to deposition results that are seldom reproducible. In particular, the honeycomb structures that have a high cell count are only poorly coated.

[0031] In addition, the resulting depositions have unsatisfactory adhesion properties. The admixture of binding agents to the catalyst powder for mitigating this problem is not desirable, since this decreases the hydrogen productivity that is achievable.

[0032] It is consequently the goal of this invention to provide a catalyst for the re-forming of alcohols, in particular methanol, with high selectivity and specific hydrogen productivity. A

palladium/zinc oxide catalysts can be clearly improved by the formation of a PdZn alloy. For the production of such a catalyst, first zinc oxide is impregnated with palladium nitrate, dried, and calcined at 500 C in air for a period of 3 hours. The PdZn alloy is formed by the reduction of the catalyst at increased temperatures. The studies of Takezawa show that the alloy formation is completed only at reduction temperatures of 500 C. Catalysts that are treated in this manner possess a very high selectivity, but a clearly lower activity than known copper/zinc oxide catalysts $Cu/ZnO/Cr_2O_3$ (30 weight percent Cu) and $Cu/ZnO/Al_2O_3$ (30 weight percent Cu). N. Takezawa describes a detailed examination of PdZn alloys in "*Selective PdZn alloy formation in the reduction of Pd/ZnO catalysts*," Bull. Chem. Soc. Jpn., 71, 1451-1455 (1998).

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[0028] The known catalysts for steam re-forming of methanol on the basis of palladium on zinc oxide show a good carbon dioxide selectivity, which can be improved further by a targeted formation of a palladium-zinc alloy. The specific hydrogen productivities determined from the published data, namely a maximum of 2.7 $Nm^3/kg \cdot h$ require further improvement, however. Besides this, the types of catalysts that are described here are powder catalysts, which are poorly suited for application in methanol re-formers in vehicles.

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[0031] In addition, the resulting depositions have unsatisfactory adhesion properties. The admixture of binding agents to the catalyst powder for mitigating this problem is not desirable, since this decreases the hydrogen productivity that is achievable.

[0032] It is consequently the goal of this invention to provide a catalyst for the re-forming of alcohols, in particular methanol, with high selectivity and specific hydrogen productivity. A hydrogen productivity of more than 20 $Nm^3/kg \cdot h$ with simultaneous carbon dioxide selectivity

of more than 95% is targeted for the catalyst at a reactor temperature of 300 C. Besides this, the catalyst should be usable at a reactor temperature up to 400 C. Another essential aspect of the invention is the suitability of the catalyst for coating of ceramic or metallic carrier bodies without the addition of binding agents that would decrease the specific productivity of the catalyst.

[0033] This objective is solved by a catalyst for the steam re-forming of alcohols that contains a palladium-zinc alloy and zinc oxide as active components. The catalyst is characterized by the fact that the catalytically active components on at least one carrier material are precipitated from the group aluminum oxide, aluminum silicate, titanium oxide, zirconium oxide, zeolite, and mixtures or mixture oxides of these.

[0034] Preferably the catalyst of this invention has the palladium/zinc alloy portion in an amount of 0.5 to 10 weight percent and the zinc oxide portion in an amount from 1 to 50 weight percent, referenced to the total weight of the catalyst. The carrier material that comes under consideration for the catalyst should have a specific BET surface (measured in accordance with DIN 66132) of more than 5, preferably more than 50 m^2/g.

[0035] The catalyst is characterized by a high hydrogen productivity of more than 20 $Nm^3/kg_{Kal} \bullet h$ at a reactor temperature of 300 C, which is not achieved by catalysts made with current state-of-the-art technology. If aluminum oxide is used as a carrier material, the catalyst shows at a temperature of 350 C a specific hydrogen productivity up to 60 $Nm^3/kg_{Kal} \bullet h$ with a simultaneous carbon dioxide selectivity of more than 95%. This good value for selectivity was not to be expected, since it is generally known that during the steam re-forming of methanol, aluminum oxide promotes the formation of dimethyl ether as a by-product (H. Takahashi et al., *Steam reforming of methanol over group VIII metals supported on SiO_2, Al_2O_3 and ZrO_2*. React. Kinet. Catal. Lett., Vol. 52, No. 2, 303-307 (1994)). In contrast to the results of this item in the literature, no formation of dimethyl ether could be observed with the catalyst of this invention.

[0036] Preferably an active aluminum oxide is selected as carrier material. Active aluminum oxides are understood to include finely distributed aluminum oxides that have the crystal structures of the so-called transition phases of aluminum oxide and that possess high specific surfaces up to 400 m^2/g. To these belong the chi-, delta-, gamma-, kappa-, theta-, and eta-aluminum oxides (see Uhlmann's *Encyclopedia of Industrial Chemistry*, fifth edition, Vol. A1, pp. 560-562, 1985). For stabilizing the aluminum oxide against thermal loads, it can be doped in a known manner with 0.5 to 10 weight percent lanthanum oxide, referenced to the total weight of the catalyst.

[0037] In a special application form of the catalyst, besides having one of the named carrier materials, it also has a finely distributed zinc oxide as a carrier material for the catalytically active components. Also in this case the catalyst contains preferably 0.5 to 10 weight percent of the palladium/zinc alloy and 1 to 50 weight percent of the zinc oxide, referenced to the total weight of the catalyst.

[0038] The catalyst can be shaped into formed bodies. Formed bodies that are suitable include tablets, pellets, extruded forms, or granulates. The catalytically active components in this case are present homogeneously throughout the cross section of the formed body. This homogeneous distribution is responsible for a large portion of the catalytically active components being used insufficiently because of the poor access for reagents. Besides this, due to the increased length of time of contact of the reagents with the catalytically active components inside the formed bodies, there is an increased danger of the formation of by-products, and thus a decrease in selectivity. It

is thus more beneficial if the carrier material is shaped into formed bodies and the catalytically active components, namely the PdZn alloy and zinc oxide, are present essentially in a surface layer shell with a thickness of 50 to 500 µm on the shaped bodies. In this way, the catalytically active components are better used and the selectivity of the catalytic conversion is improved.

[0039] Preferably, the catalyst of this invention is used in the form of a deposit of carrier bodies made of ceramic or metal. Particularly well suited for this are the familiar honeycomb bodies used in auto exhaust treatment with cell densities (number of flow channels per cross section area) of more than 10 cm^{-2}. In contrast to the known catalysts of PdZn/ZnO alloys without a carrier body, using the coated alloy catalyst of this invention one can produce a tightly bonded layer on the usual carrier bodies for catalysts without using additional binding agents. The familiar carrier bodies include metal sheets, heat exchanger plates, ceramic or metallic foam bodies, and irregularly shaped components.

[0040] Essential for the catalyst of this invention is the complete alloy formation to the extent possible between palladium and zinc, whereby excess zinc is present in the catalyst as zinc oxide. Alloy formation that is as complete as possible can be guaranteed with familiar methods during the production of the catalyst.

[0041] One possibility for the manufacture of the catalyst of this invention consists of the fact that the carrier material of the catalyst can be impregnated with a common aqueous solution of soluble compounds of zinc and palladium, dried, and the catalyst preliminary stage calcined at temperatures between 300 and 550 C in an oxidizing atmosphere, and finally reduced at temperatures between 350 and 500 C in a gas that contains hydrogen.

[0042] The calcination temperature following impregnating of the carrier material must be selected such that the soluble compounds of zinc and palladium are decomposed to the corresponding oxides. For this it is sufficient to apply temperatures of at least 300 C. Temperatures above 550 C should be avoided, however, since with increasing temperature there is a danger of the formation of a spinel between the carrier material and the zinc oxide, in particular during the use of aluminum oxide. The length of time of calcination is selected so that the compounds of the zinc and palladium are decomposed as completely as possible. This is achieved, depending on the temperature selected, after 1 to 5 hours.

[0043] After calcinations the catalyst is reduced at temperatures between 350 and 500 C, preferably between 350 and 450 C, in a gas that contains hydrogen. Here the palladium-zinc alloy forms. As detailed studies have shown, the alloy formation is made easier when the carrier material is simultaneously impregnated with the zinc and palladium compound and then calcined. A sequential impregnation of the carrier material with both compounds and intermediate calcinations leads to worse hydrogen productivities and carbon dioxide selectivities during steam re-forming, which can be explained only by an incomplete alloy formation between zinc and palladium.

[0044] For zinc and palladium compounds, nitrate and acetate are particularly well suited, as their oxide remnants can be removed completely during calcination. During production of the alloy catalyst in the form of a catalyst powder, even economical chloride palladium compounds can be used, since the chlorine can be removed from the powder catalyst relatively easily by repeated washing.

[0045] The production method described can be applied to a carrier material existing as a

finely distributed powder. The post-treatment deformation of the resulting catalyst material would lead, however, to a homogeneous distribution of the catalytically active components over the cross section of the formed bodies, with the above described disadvantages. It is therefore better to shape the carrier material first and then impregnate it with the catalytically active compounds. This leads to the condition that the catalytically active components are deposited essentially within a surface shell with a thickness in the range of 50 and 500 μm on the formed bodies.

[0046] To produce a coating catalyst on a carrier body, this is best coated first with the carrier material and the coating is then impregnated simultaneously with the two catalytically active compounds. Following this impregnation is the above described process of drying, calcining, and reduction of the coating.

[0047] To produce a catalyst that contains zinc oxide as another carrier material, zinc oxide, together with at least one carrier material from the group aluminum oxide, aluminum silicate, titanium oxide, zirconium oxide, zeolite, and mixtures of these or mixture oxides of these, is dispersed in water. The resulting dispersion is a base. To this basic dispersion one adds an acidic solution of a palladium compound. Next the dispersion is neutralized at high temperature with a base, such as sodium carbonate for example, and then while the temperature is maintained it is reduced using an aqueous reducing agent, filtered off, washed, dried, calcined at temperatures between 300 and 500 C in an oxidizing atmosphere and finally reduced at temperatures between 350 and 500 C, preferably between 350 and 450 C, in a gas containing hydrogen. For an aqueous solution, one can use a solution of formaldehyde and sodium hydroxide. Neutralization and reduction are conducted preferably at temperatures of dispersion between 50 and 90 C, in particular between 70 and 90 C.

[0048] As an alternative to this, the catalyst material can simply be washed after the post-chemical reduction and filtration, and then dispersed again. With the aid of this dispersion, then, a carrier body is coated with catalyst material. To finish the coated catalyst, the coating is dried, calcined at temperatures between 300 and 550 C in an oxidizing atmosphere, and finally reduced at temperatures between 350 and 500 C in a gas containing hydrogen.

[0049] Surprisingly, using this method the palladium is also completely alloyed with zinc, which is recognized in the good carbon dioxide selectivity of a catalyst produced in this manner, although no soluble zinc compound is added to the dispersion, which could be precipitated out simultaneously with the palladium compound. Apparently by the input of the acid metal solution the zinc oxide, which is added as a finely distributed powder, is partially dissolved. During neutralization of the dispersion with sodium carbonate, then palladium and the zinc that has gone into solution precipitates both on the zinc oxide as well as on the other carrier material. The good results for the carbon dioxide selectivity of such a catalyst indicate that during the reduction steps the palladium has formed an alloy completely with zinc during the manufacture of the catalyst.

[0050] The following examples and comparative examples serve only as further explanation of the invention. Several catalysts in accordance with this invention and several comparison catalysts were produced. The examination of the catalysts took place in a reactor heated using electricity, shown in Figure 1.

[0051] In Figure 1, item (1) is the reactor, item (2) is a reaction tube arranged in the reactor, and item (3) is a heating mantle with two heating elements (10) and (11). In the reaction tube (2)

there is in the lower portion an evaporator unit (4), which consists of a pile of glass beads and is heated by a heating element (11). In the condenser (6) there is a mixture of water and methanol that is distributed via a fluid pump (7) over the heated glass beads and is evaporated. The mix of methanol and water that arises therefrom is led upward across a probe (5) of the catalyst to be examined, which is heated by heating element (10). In Figure 1 there is an illustrative example of a probe of a honeycomb coated with a catalyst to be examined. The product gas mixture is removed from the head of the reactor and fed into the condenser (8), in which the condensable components of the product gas are liquefied and separated from the gas phase in the trap (9). The separated gas phase is analyzed with the help of gas chromatography to determine its components. At the lower end of the reactor (1) a carrier gas can be fed for the methanol steam mixture.

[0052] The catalysts of the following examples and comparative examples were all examined at a stoichiometric ratio of water to methanol of 1.5 (steam-to-carbon ratio = SC = 1.5) and a volume rate of LHSV = 5 h^{-1} (LHSV = liquid hourly space velocity), referenced to the material. The carbon dioxide selectivity S_{CO2} in accordance with Equation (5) was determined for different reaction temperatures, the concentration of carbon monoxide in the dry product gas, as well as the specific hydrogen productivity P_{Kat} in accordance with Equation (4) was determined, referenced to the catalyst mass (without the mass of the given carrier body used), and the specific hydrogen productivity P_{Pd}, referenced to the mass of the palladium used.

[0053] The results are given in tables 1 to 5.

Example 1

[0054] A coating catalyst A was produced as follows on a honeycomb body.

[0055] A ceramic honeycomb body with 62 cells per cubic centimeter and a volume of 0.063 liter was coated with 7.25 g of gamma-aluminum by dipping into an aqueous dispersion of gamma-aluminum oxide (specific area: 140 m^2/g) and calcining over 2 hours at 600 C. Following calcining, the coated honeycomb was impregnated by dipping into a solution containing zinc nitrate and palladium nitrate (113.4 g $Pd(NO_3)_2$ and 768.5 g $Zn(NO_3)_2 \cdot 6 H_2O$ in 1 liter of water). After calcining for 2 hours at 500 C in air, the coated honeycomb body was reduced for 2 hours at 400 C under flowing form gas (95 volume percent N_2 and 5 volume percent H_2).

[0056] The catalytically active coating of the catalyst produced in this manner had a total weight of 8.78 g, corresponding to 139.3 g per liter volume of the honeycomb body. It contained 5.8 weight percent PdZn alloy, 11.6 weight percent ZnO and 82.6 weight percent Al_2O_3, referenced in each case to the total weight of the catalytically active coating.

Table 1.: Re-forming results for catalyst A.

T C	S_{CO2} %	CO Concentration in Product Gas (Vol.-%)	P_{Kat} $Nm^3/kg_{Kat} \cdot h$	P_{Pd} $Nm^3/k_{Pd} \cdot h$
300	97	0.7	37.8	0.8
350	95	1.2	60.7	1.3
400	95	1.2	66.2	1.4

Example 2

[0057] A powder catalyst B was produced as follows.

[0058] A batch of 125 g of catalyst carrier (gamma-aluminum oxide, spheres, 2 to 4 mm diameter, specific surface 100 m^2/g) was impregnated with 0.088 liter of an aqueous solution of 2.49 g $Pd(NO_3)_2$ and 137 g $Zn(NO_3)_2 \cdot 6\ H_2O$ according to the principle of pore volume impregnation, and dried for 15 minutes at 80 C. Here the volume of the solvent used was about that of the water take-up capacity of the carrier material. Finally the impregnated catalyst carrier was calcined for 3 hours at 500 C and then reduced in flowing form gas at 400 C for 2 hours.

[0059] The finished catalyst contains 1.2 weight percent PdZn alloy, 22.4 weight percent ZnO and 76.6 weight percent Al_2O_3, each referenced to the total weight of the pellet catalyst. The Pd alloy and zinc oxide are arranged in this catalyst essentially in a surficial shell of about 250 µm thickness.

Table 2: Re-forming results for catalyst B.

T C	S_{CO2} %	CO Concentration in Product Gas (Vol.-%)	P_{Kat} $Nm^3/kg_{Kat} \cdot h$	P_{Pd} $Nm^3/k_{Pd} \cdot h$
220	95	1.2	1.0	0.1
300	95	1.2	3.4	0.7
350	96	1.0	8.2	1.2
400	93	1.8	9.4	1.3

[0060] The catalysts A and B were produced by co-impregnation of aluminum oxide with palladium and zinc nitrate. In both catalysts comparable selectivity was achieved, whereby at 400 C one can observe a worsening in the pellet catalyst. A possible explanation for this is as follows. In the pellet catalyst B it is a matter of a shell catalyst with a shell thickness of about 250 µm. The core of the catalyst consists almost exclusively of pure aluminum oxide. At a higher temperature the possibility also increases that the reaction agents diffuse in the core of the catalyst. The contact of methanol with the pure aluminum oxide, however, leads to undesired secondary reactions that decrease the selectivity.

[0061] The catalysts show distinct differences with respect to hydrogen productivity per kilogram of catalyst and hour. The low values in pellet catalyst B are explained by the high ratio of catalytically inactive carrier material in the core of the pellet. The determination of the hydrogen productivity per gram of palladium confirms this assumption. It is approximately the same for both and shows that the catalytically active core components of the pellet catalyst are located completely in a surface shell that is easily accessible for the reaction agents.

Example 3

[0062] A coated catalyst C was produced as follows.

[0063] A dispersion was made of 36.6 g gamma-aluminum oxide (specific surface 140 m^2/g) and 11.9 g ZnO in 400 ml of water, into which a solution of 5.88 g H_2PdCl_4 in 100 ml of water was added. The dispersion was heated to 80 C and neutralized with sodium carbonate. Next at

180 C 12 ml of an aqueous solution of 1.65 g formaldehyde and 0.6 g sodium hydroxide was added. After stirring for 15 minutes the dispersion was filtered off and washed three times with 500 ml of water. The residue obtained was redispersed with 250 l of water.

[0064] A ceramic honeycomb body with 62 cells per cubic centimeter and a volume of 0.63 liter was dipped into the coating dispersion obtained above and coated with 6.3 g of material after 2-hour calcinations at 400 C. Next the honeycomb body was reduced for 2 hours at 400 C under form gas.

[0065] The catalytically active coating of catalyst C had the following composition: 8.1 weight percent PdZn alloy, 19.7 weight percent ZnO and 72.2 weight percent Al_2O_3, each referenced to the total weight of the coating.

Table 3. Re-formation results for catalyst C.

T C	S_{CO2} %	CO Concentration in Product Gas (Vol.-%)	P_{Kat} $Nm^3/kg_{Kat} \cdot h$	P_{Pd} $Nm^3/k_{Pd} \cdot h$
300	97	0.7	24.3	0.5
350	98	0.5	40.8	1.2
400	97	0.7	51.9	1.3

[0066] Catalyst C is characterized by very high selectivity and corresponding low CO content in the re-format. However, compared to catalyst A it has a very low hydrogen production.

Comparative Example 1

[0067] A pellet catalyst D was produced as follows.

[0068] A quantity of 100 g of zinc oxide tablets was impregnated with 0.030 liter of an aqueous solution of 2.49 g $Pd(NO_3)_2$ according to the principle of pore volume impregnation and dried for 15 minutes at 80 C. Next the pretreated catalyst carrier was calcined at 500 C for 3 hours and finally reduced at 400 C for 2 hours in form gas.

[0069] Catalyst D consisted of 1.8 weight percent PdZn alloy and 98.2 weight percent ZnO.

Table 4: Re-forming results for catalyst D.

T C	S_{CO2} %	CO Concentration in Product Gas (Vol.-%)	P_{Kat} $Nm^3/kg_{Kat} \cdot h$	P_{Pd} $Nm^3/k_{Pd} \cdot h$
220	82	4.5	0.11	0.024
300	78	5.5	0.60	0.13
350	79	5.3	0.85	0.19
400	81	4.8	1.22	0.27

[0070] Catalyst D shows a very low hydrogen productivity, which can be explained by the high ratio of zinc oxide that is difficult to access. Surprisingly, the selectivity achieved clearly lags behind the powder catalysts known from the literature.

Comparative Example 2

[0071] A coated catalyst E was produced as follows.

[0072] A ceramic honeycomb body with 62 cells per cubic centimeter and a volume of 0.063 liter was coated with 7.25 g of gamma-aluminum oxide by dipping in an aqueous dispersion of gamma-aluminum oxide (specific surface of 140 m^2/g) and subsequent calcination for 2 hours at 600 C. Next the coated honeycomb body was impregnated by dipping into a solution containing zinc nitrate (768.5 g of $Zn(NO_3)_2 \cdot 6\ H_2O$ in 1 liter of water).

[0073] After calcination for 2 hours at 500 C the honeycomb body was impregnated by dipping into an aqueous solution of palladium nitrate (113.4 g of $Pd(NO_3)_2$ in 1 liter of water), calcined for 2 hours at 500 C and reduced for another 2 hours at 400 C in form gas.

[0074] The catalytically active coating of catalyst E has the following composition: 3.5 weight percent palladium, 14.3 weight percent ZnO and 82.2 weight percent Al_2O_3.

Table 5. Re-formation results for catalyst E.

T C	S_{CO2} %	CO Concentration in Product Gas (Vol.-%)	P_{Kat} $Nm^3/kg_{Kat} \cdot h$	P_{Pd} $Nm^3/k_{Pd} \cdot h$
300	55	11.3	12.7	0.3
350	60	10.0	25.1	0.6
400	64	9.0	26.3	0.7

[0075] As the results in Table 5 show, catalyst E delivers both a lower hydrogen productivity and a decreased selectivity compared to catalyst A. These differences probably are based on the fact that catalyst A was produced by co-impregnation of the aluminum oxide coating with palladium nitrate and zinc nitrate, while catalyst E was produced by sequential impregnation of the aluminum oxide coating. Apparently the co-impregnation of palladium and zinc makes it easier for the formation of the PdZn alloy.

[0076] The catalyst of this invention is suitable for steam re-forming of alcohols in accordance with reaction equation (1) and also for autothermic steam re-forming of alcohols. In these methods the gas-forming educt stream is mixed with an oxygen-containing gas mixture. The energy necessary for the endothermic steam re-forming is made available by a partial oxidation of methanol in the reactor.

Patent Claims

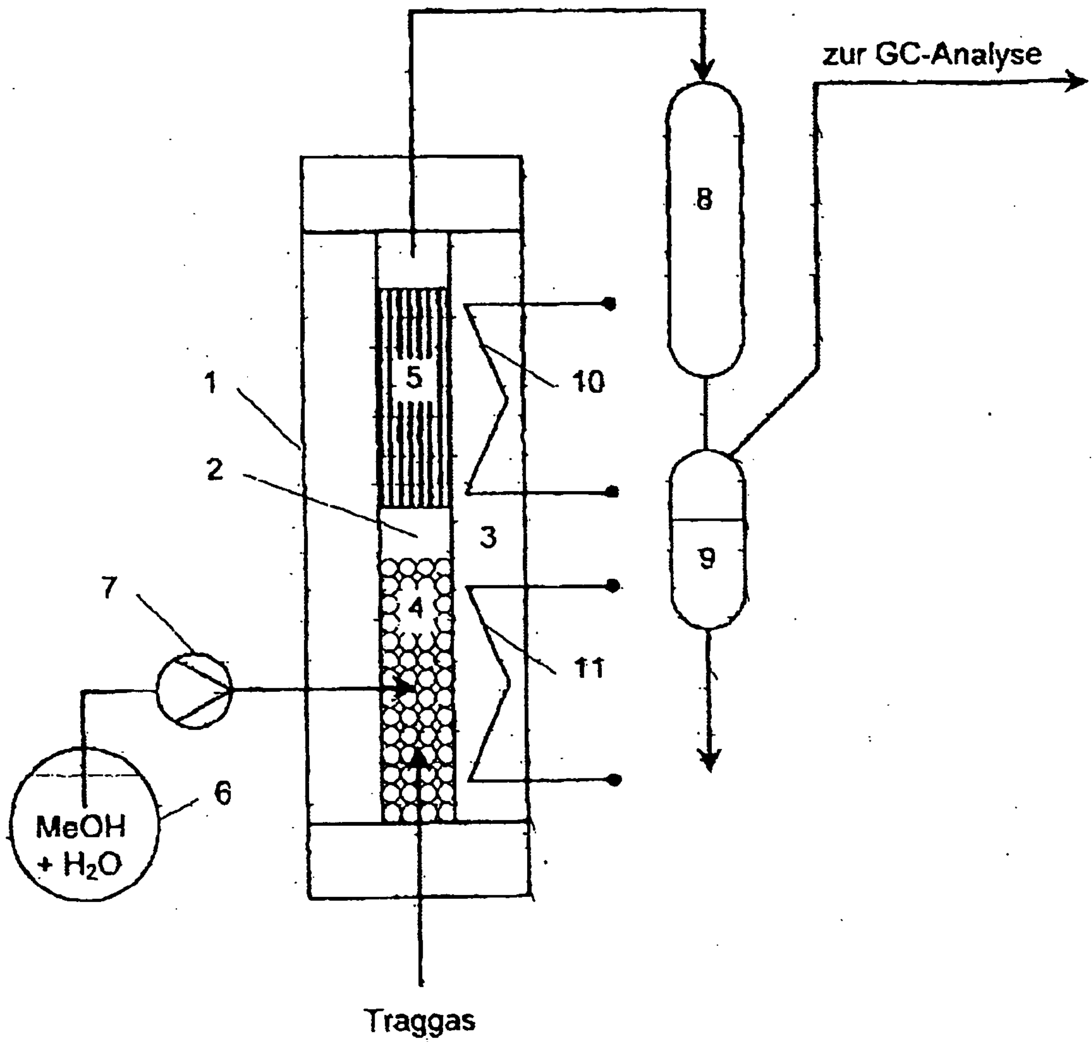
1. Catalyst for the steam re-forming of alcohols, containing a palladium-zinc alloy and zinc oxide as catalytically active components, characterized by the fact that the catalytically active components are precipitated on at least one carrier material from the group aluminum oxide, aluminum silicate, titanium oxide, zirconium oxide, zeolite and mixtures or mixed oxides of the same.

2. Alloy catalyst according to claim 1, characterized by the fact that it contains 0.5 to 10 weight percent of palladium-zinc alloy and 1 to 50 weight percent of zinc oxide, each referenced to the total weight of the catalyst.

3. Alloy catalyst according to claim 2, characterized by the fact that during the steam reforming of methanol it has a hydrogen productivity of more than 20 Nm^3/kg at a reactor temperature of 300 C.
4. Alloy catalyst according to claim 1, characterized by the fact that the carrier material is an aluminum oxide with a specific surface of more than 10 m^2/g.
5. Alloy catalyst according to claim 1, characterized by the fact that the aluminum oxide is stabilized against thermal loads with 0.5 to 10 weight percent of lanthanum oxide, referenced to a total weight of aluminum oxide and lanthanum oxide.
6. Alloy catalyst according to claim 1, characterized by the fact that zinc oxide is present as an additional carrier material for the catalytically active components.
7. Alloy catalyst according to claim 6, characterized by the fact that it contains 0.5 to 10 weight percent of palladium-zinc alloy and 1 to 50 weight percent of zinc oxide, each referenced to the total weight of the catalyst.
8. Alloy catalyst according to claim 1, characterized by the fact that it is shaped into form bodies.
9. Alloy catalyst according to claim 1, characterized by the fact that the carrier material is shaped into form bodies and the catalytically active components are present in a surface shell with a thickness of 50 to 500 μm on the form bodies.
10. Alloy catalyst according to claim 1, characterized by the fact that it is present in the form of a coating on a carrier body.
11. Method for production of an alloy catalyst according to claim 1, characterized by the fact that the carrier material is impregnated with a common aqueous solution of soluble compounds of zinc and palladium, is dried, and the thus obtained catalyst preliminary stage is calcined at temperatures between 300 and 550 C in an oxidizing atmosphere, and then reduced at temperatures between 350 and 500 C in a gas containing hydrogen.
12. Method according to claim 11, characterized by the fact that the carrier material is introduced in the form of a powder.
13. Method according to claim 12, characterized by the fact that the alloy catalyst is worked into a form body.
14. Method according to claim 11, characterized by the fact that the carrier material is introduced shaped into a form body.
15. Method according to claim 11, characterized by the fact that the carrier material is present as a coating on the carrier body.
16. Method for production of an alloy catalyst according to claim 6, characterized by the fact that zinc oxide, together with at least one carrier material from the group aluminum oxide, aluminum silicate, titanium oxide, zirconium oxide, zeolite, and mixtures or mixed oxides of the same, is dispersed in water and that an acidic solution of a palladium compound is added to the resultant basic dispersion, and then the dispersion is neutralized with a base at increased temperature, and while maintaining the temperature is reduced with an aqueous reduction agent, filtered off, washed, dried, calcined at temperatures between 300 and 550 C in an oxidizing atmosphere, and then reduced at temperatures between 350 and 500 C in a

gas containing hydrogen.

17. Method according to claim 16, characterized by the fact that the alloy catalyst is shaped into form bodies or is applied as a coating to a carrier body.
18. Method for production of an alloy catalyst according to claim 6, characterized by the fact that zinc oxide, together with at east one carrier material from the group aluminum oxide, aluminum silicate, titanium oxide, zeolite, and mixtures or mixed oxides of the same, is dispersed in water and that an acidic solution of a palladium compound is added to the resultant basic dispersion and that next the dispersion is neutralized with a base at an increased temperature, and while maintaining the temperature is reduced with an aqueous reduction agent, filtered off, washed, dried, once again dispersed in water and applied in the form of a coating to a carrier body, calcined at temperatures between 300 and 550 C in an oxidizing atmosphere, and then reduced at temperatures between 350 and 500 C in a gas containing hydrogen.
19. Application of the alloy catalyst according to claims 1 through 8 for the steam re-forming of methanol.
20. Application of the alloy catalyst according to claims 1 through 8 for the autothermal steam re-forming of methanol.



Figur 1